1934

Titanous Chloride as a Standard Reducing Agent

Alfred R. Armstrong
College of William & Mary - Arts & Sciences

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SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS

OF

THE COLLEGE OF WILLIAM AND MARY

for the degree

MASTER OF ARTS

1 9 3 4

ACKNOWLEDGMENT

The author takes this opportunity to express his grateful appreciation for the advice and assistance given by Dr. A. W. Dearing under whom this work was carried out.

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INTRODUCTION

Discovery of Titanium

Rev. William Gregor, a priest of the parish of Menachan, in Cornwall, England, found there a black sand, occurring in great abundance, which he found to be composed of the oxides of iron and of a new metal. The date of his discovery is given as 1789 (1) and as 1791 (2). The sand was named "menakanite".

In 1795 M. H. Klaproth extracted an oxide from the "red schorl" (rutile) of Hungary. In 1797 he identified the oxide of menakanite with rutile. The name "titanic earth" (Latin, titanes, sons of the earth), applied by Klaproth to the oxide, has remained the basis of our name for the element.

Occurrence and Distribution in Nature

Far from being the rare element that it is usually considered to be, titanium is believed to be five times as plentiful as phosphorus and nine times as plentiful as sulphur. According to Clarke (3) it makes up about 0.58% of the known terrestrial matter. Most igneous rocks contain titanium; and it is widely distributed in soils and clays. It has been found in peats and in the ashes of certain coals. Ashes of oak, apple, and pear woods give a test for the element. Thalen discovered its spectral lines in light from the sun in 1868; and it has since been identified in many stars.

In minerals titanium usually occurs either as the dioxide or as titanates. Rutile is the pure dioxide, likewise octahedrite and Brookite. The Menaccanite of Gregor, now usually called Ilmenite, is believed to be ferrous titanate, $FeTiO_3$, rather than iron titanium sesquioxide $(Fe,Ti)_2O_3$ as it was formerly regarded. Analyses of the mineral show no definite composition. Iron is nearly always present in both conditions of valence; the formula $mFeTiO_3nFe_2O_3$ is used to express its composition in a general way. The other titanium bearing minerals are not found in sufficiently large deposits to make them of economic importance. A list of these minerals containing titanium, either as an essential or accidental ingredient, as well as descriptions of the commercially important ores has been compiled by Thornton (4).

General Chemistry of Titanium

Classified according to the periodic system of Mendeleef, titanium is in Group IV A. The typical elements, carbon and silicon, form hydrides which is characteristic of the B family. Thus titanium is the first member of the A family which includes zirconium, hafnium, and thorium. The differences in the A and B families reach a minimum in Group IV. It is to be noticed that the elements in A are slightly more electropositive than those in B; also, there is an increase in metallic character from titanium to thorium. This may be shown from the hydrolysis of the salts or the acidity of the oxides. Titanium may be determined quantitatively by the hydrolysis of its salts; analogous zirconium salts are hydrolized with greater difficulty; and, thorium salts are more stable than those of zirconium. Titanium dioxide is amphoteric, acidic proper-

ties end with zirconium dioxide, and thorium dioxide forms a fairly strong base. Members of this sub-group form peroxides as do the elements of Group III A. Alkali salts of H_2XF_6 are characteristic of all members of the fourth group except carbon.

Early values for the atomic weight of titanium were inaccurate. In 1808 Dalton gave the value Ti = 40 (O = 7). Berzelius, 1813, using O = 100, suggested 1801.0. Of historical interest is the work of Rose, Mosander, Pierre, and Demoly from 1813 to 1830. Thorpe, 1883-5, hydrolyzed the pure tetrachloride or tetrabromide, and determined the titanic oxide and the halogen hydracid. On the basis of Thorpe's work the International Committee on Atomic Weights adopted the value Ti = 48.1 in 1917. Baxter and Fertig (5) about 1922 worked with the tetrachloride and tetrabromide, applying all refinements to the analyses. The work was continued by Baxter and Butler (6) who gave their final report in 1926. The International Committee on Atomic Weights accepted their value, and since 1927 the accepted atomic weight has been 47.90.

Titanium forms three series of salts depending upon its valence. Only the quadri-valent compounds are stable in air; but both the di- and ter-valent compounds are well known.

Titanium difluoride is unknown; the trifluoride is not uncommon; and the tetrafluoride not only exists, but forms complex salts of the form K_2TiF_6.

Three chlorides of titanium are known $TiCl_2$, $TiCl_3$, and $TiCl_4$. Titanic chloride forms complex and basic salts. The trichloride is most important from the point of view of analytical work. It was first obtained in the anhydrous state by Ebelmen, who passed a mixture of hydrogen and the

vapour of the tetrachloride through a red hot tube and found the trichloride deposited in the cold part of the tube. At 1200°C 94% of the tetrachloride was decomposed. The trichloride is formed when $TiCl_4$ is heated to 200°C with silver in a sealed tube. Numerous other methods for the reduction of quadri-valent titanium have been suggested (7).

It was observed by Ebelmen that titanium trichloride was a powerful reducing agent. Knecht and Hibbert (8) have studied its use in this capacity extensively. In this country Thornton has checked much of their work.

Bromides of only two valences have been found. Titanium dibromide is unknown. All three iodides are known.

TiO, Ti_2O_3, and TiO_2 may be formed. The sesquioxide is basic, giving rise to salts; the dioxide is acidic, forming titanates as well as a few salts.

Sulphides and sulphates corresponding to each of the three valence states have been prepared. The sesquisulphate is more easily prepared than the trichloride, hence is often used as a standard reducing agent.

The chemistry of the compounds of titanium with nitrogen, phosphorus, carbon, and silicon are given in much detail by Friend (9).

Much controversy has taken place concerning the valence of titanium in the trioxide, TiO_3, and in the per-salts. A compound of the formula $Ti(OH)_6$ or $TiO_3 \cdot 3H_2O$ has been isolated. Faber (10) was led to the conclusion by his work that titanium is hexivalent in such compounds. Since sub-group A normally forms peroxides, it seems unnecessary to give up our belief that four is the maximum valence of Group IV elements just to care for this case.

Reactions of Analytical Value

Ebelmen showed that ferric salts were reduced by titanium trichloride to ferrous salts. This reaction is quantitative and takes place in the cold. This was worked out by Knecht and Hibbert (11) and published in 1903. The reaction is simply

$$TiCl_3 + FeCl_3 = TiCl_4 + FeCl_2$$

This furnishes a method for determining either ferric iron or trivalent titanium.

Titanium may also be estimated by means of a standard solution of methylene blue. A titanic salt is reduced by zinc and hydrochloric acid, and the solution titrated in a current of carbon dioxide with standard methylene blue solution until a permanent blue color shows the complete oxidation of the titanium.

In addition to zinc and hydrochloric acid, numerous other methods have been devised for the reduction of the titanic salts. Zinc and sulphuric acid work but require more time. The Jones reductor filled with amalgamated zinc has proved satisfactory. Cadmium (12) powder in the Jones reductor serves to reduce ferric sulphate to ferrous sulphate and $Ti(SO_4)_2$ to $Ti_2(SO_4)_3$ quantitatively. The reaction is faster than with zinc and there is less evolution of hydrogen. Morley and Wood (13) have successfully used aluminum foil and hydrochloric acid.

A mixture of titanium and iron may be reduced and titrated electrometrically for both titanium and for iron. If the apparatus for electrometric titration is not at hand, standard methylene blue may be used to oxidize the titanium, since there is no reaction between the ferrous solution and methylene blue. Thornton (14) has shown that the titanium can be precipitated quantitatively from a mixture of titanic and ferric

chlorides by means of nitrosophenyl hydroxylamine (cupferon).

A cupric salt in a solution free from nitric or chloric acids may be reduced to the cuprous salt by the addition of titanous chloride. The cuprous salt settles out as a white precipitate. A known quantity of ferric salt is introduced along with an excess of potassium thiocyanate which serves as an indicator. The whole of the copper is reduced before the ferric iron is attacked. The disappearance of the red ferric thiocyanate indicates the complete reduction of iron and copper. The reduction of the copper may be represented by the following equation:

$$2CuCl_2 + 2TiCl_3 = Cu_2Cl_2 + 2TiCl_4$$

A simplification of this determination consists of adding an excess of ferrous ammonium sulphate to the cupric solution and titrating the ferric iron formed with titanium trichloride using potassium thiocyanate as an indicator.

The methods for molybdenum were worked out (15) with the object of applying them, if successful, to the indirect determination of phosphoric acid. This work was continued by Thornton (16). He found that molybdic acid was quantitatively reduced to $MoCl_3$ by zinc and hydrochloric acid. The molybdenum was titrated using standard methylene blue solution with the color changes salmon pink, light yellow, light green, dark green, blue green. The salmon pink $MoCl_3$ is first converted to yellow $MoCl_4$; the light green shows the formation of $MoCl_5$; and, the blue green indicates the end point corresponding to the conversion of all of the molybdenum to the pentavalent condition. The quantity of $MoCl_5$ allowable in the

solution is limited by its green color which tends to obscure the end point. Since in ammonium phosphomolybdate one milligram of phosphorus corresponds to 37.14 mg. of molybdenum, only exceedingly small quantities of phosphorus may be determined by this method.

Willard and Fenwick (17) have reduced molybdic acid using standard titanous chloride solution. More of the reducing agent is used than is called for by theory if the reduction proceeds to $MoCl_5$; a correction factor must be applied to the volume of reducing agent used. The reaction is slow and the voltage change in the electrometric titration is not free from transient variations.

Salts of chromic acid are quantitatively reduced to chromic salts by titanous chloride. Since chromic acid oxidizes potassium thiocyanate, it is necessary to add excess titanous chloride then add the indicator and back titrate using ferric alum solution.

The addition of titanous chloride to an excess of hydrogen peroxide gives the yellow or orange color of TiO_3. As the titanous chloride is added to the yellow solution, the TiO_3 is reduced according to the equation:

$$TiO_3 + 2TiCl_3 + 6HCl = 3TiCl_4 + 3H_2O$$

Two molecules of titanous chloride are required for one of hydrogen peroxide.

Chlorates are reduced in the cold by titanous chloride according to the equation:

$$KClO_3 + 6TiCl_3 + 6HCl = KCl + 6\,TiCl_4 + 3H_2O$$

Perchlorates are reduced by concentrated $Ti_2(SO_4)_3$ or by $TiCl_3$ provided the reducing agent is introduced in excess. The excess may be determined using standard iron alum solution.

Persulphates are reduced quantitatively provided an excess of the titanous chloride is present according to the equation:

$$KSO_4 + TiCl_3 + HCl = KHSO_4 + TiCl_4$$

The excess reducing agent may be determined using standard iron alum.

In the estimation of nitrates, titanous chloride may be used to determine the ferric iron produced by the action of the nitric acid on ferrous sulphate:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

In the presence of caustic alkali, nitrates are reduced to ammonia. The ammonia may then be determined by the Kjeldahl method. Nitrites may be determined similarly.

The following list of nitro compounds are quantitatively reduced in acid solution by titanous chloride: Paranitraniline, nitrobenzene, picric acid, dinitrobenzene, trinitrotoluene, and dinitrotoluene. In every case the nitro groups are reduced to amino groups. Nitroso compounds behave similarly.

Diazo compounds in dilute hydrochloric acid solution are reduced; two molecules of titanous chloride are required for each molecule of the diazo compound. The following equation shows the reduction of benzene diazonium chloride to diazobenzene phenylhydrazide:

$$2C_6H_5N_2Cl + 4TiCl_3 + 2HCl = C_6H_5N{:}\ N{\cdot}NC_6H_5{\cdot}NH_2 + 4TiCl_4$$

Many dyestuffs may be determined by the use of titanous chloride. In addition to the nitro and azo dyes, there are many which yield colorless leuco compounds. Methylene blue, indigo, thioindigo red, and pararosaniline hydrochloride belong to this group.

Alizarin in alcholic solution is reduced; four molecules of titanous chloride are required for each molecule of the dyestuff. This, like the other dyes mentioned, may be estimated in dyed cotton fabric.

EXPERIMENTAL PART

Statement of the Problem

This work was undertaken in order to determine:

(1) whether or not the procedures involved in the use of titanium compounds might be applied effectively in a course in elementary quantitative analysis;

(2) the validity of Zintl's (18) defense of copper sulphate as a primary standard for titanous solutions;

(3) the best experimental conditions under which phosphorus may be indirectly determined by the titanium trichloride method.

The Materials and Methods Used

Materials

The titanous chloride used was secured from the LaMotte Chemical Products Co., Baltimore, Md. in the form of a 20% solution. It was found free from sulphide and iron. The fraction oxidized to $TiCl_4$ was negligible.

The nethylene blue came from The Coleman and Bell Co., Norwood, Ohio. It contained no impurities which obscured the end point.

Special sodium oxalate for standardizing according to Sörensen (Lot No. 8532) made by the J. T. Baker Chemical Company was used as a primary standard for potassium permanganate.

Special fine crystal ferrous ammonium sulphate hexahydrate made by the J. T. Baker Chemical Company was used as a primary standard for titanous chloride.

"Baker's Analyzed" special large crystal cupric sulphate (Lot No. 6132) was used in all experiments requiring that reagent.

Iron wire labeled "No. 30 For Standardizing" supposed to contain 99.8% iron was found unsuitable for use as a primary standard without preliminary oxidation with permanganate and reduction with zinc. The label failed to bear the name of the maker or distributor.

Where there was no need for chemicals of great purity the general stockroom supply of reagents was used without special note of specifications or manufacturer.

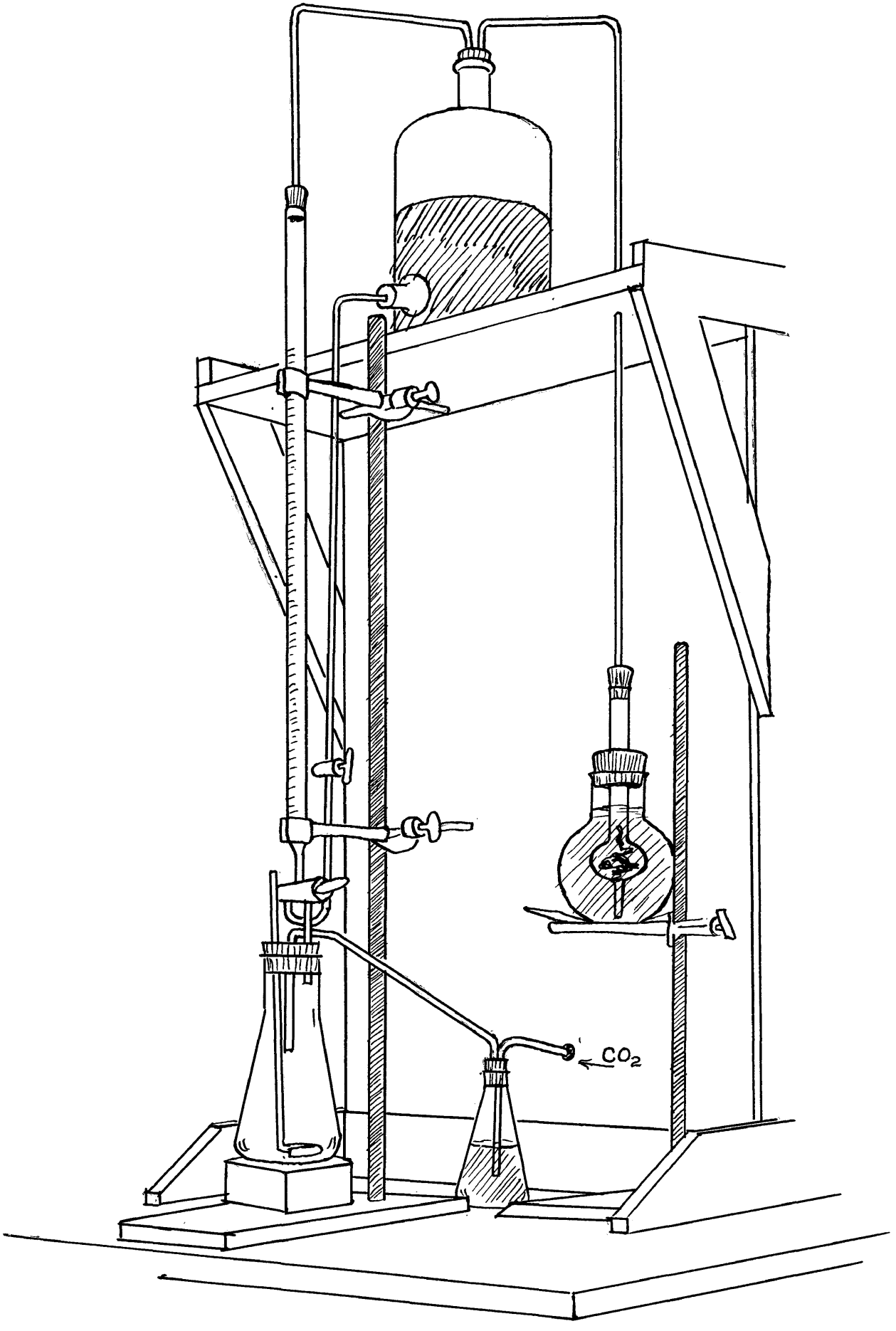
Methods

Preparation of the Solution of Titanous Chloride

The solution of titanous chloride used in these experiments was prepared in accordance with the directions given by Knecht and Hibbert (21). A large quantity was prepared in order to carry out a larger number of titrations and at the same time to determine its stability over a long period of time.

Apparatus

The apparatus employed for storing and using the titanous chloride was modeled after that of Knecht and Hibbert (22) with the improvements proposed by Thornton and Chapman (23). A diagram of the apparatus follows this page. The lower outlet of the storage bottle is fitted with a rubber stopper through which a piece of glass tubing passes. The tubing is bent downwards; it is connected to a glass stopcock which is connected to the inlet of a buret with a three-way stopcock. Through the two-holed stopper in the top of the storage bottle pass a glass tube leading to the top of the buret and a glass tube leading to a small hydrogen generator. The hydrogen generator consists of a wide mouth bottle filled with six molar hydrochloric acid, into which dips a calcium chloride tube with the narrow aperture at the bottom, and fitted at the top with a one-holed rubber stopper to receive the tube from the storage bottle. The calcium chloride tube is filled with mossy zinc which is attacked by the hydrochloric acid as soon as the solution is drawn from the buret. This maintains in the storage bottle an atmosphere of hydrogen under a pressure slightly greater than atmospheric.


CO_2

All air is expelled from the apparatus by flushing with hydrogen or carbon dioxide.

Standardization of the Titanous Chloride Solution with Ferrous Ammonium Sulphate

A sample of ferrous ammonium sulphate hexahydrate is dissolved in dilute sulphuric acid. A portion of this solution corresponding to a 40 cc. litre of titanous chloride is measured out and oxidized with dilute (N/20) potassium permanganate. The slight excess of oxidizing agent is destroyed by boiling the solution. A large excess of ammonium thiocyanate solution is added, and the ferric iron is titrated with titanous chloride until the red color of the ferric thiocyanate is completely discharged.

The ferrous solution may be made alkaline with ammonia and an excess of hydrogen peroxide added to oxidize the iron. The excess of oxygen is driven off by boiling for ten minutes. An excess of hydrochloric acid is added to dissolve the ferric hydroxide.

Methylene blue may serve as indicator in place of the ammonium thiocyanate. A very small quantity of the indicator should be used in this case since it uses up titanous chloride in becoming decolorized. The titration should be carried out above 35°C in order that the decolorization of the indicator may be instantaneous. The addition of a drop of 10% sodium salicylate solution produces a sharp end point at room temperature.

Two liters of ferric ammonium alum approximately the same strength as the titanous solution may be prepared by dissolving the alum in 0.5 molar sulphuric acid. This solution keeps indefinitely. It may be

standardized against permanganate or against the titanous chloride solution. It serves as a quick and precise method for checking the value of the reducing solution.

Standard Methylene Blue Solution

The pure dyestuff is 2:8 tetramethyldiaminothiazoniumchloride ($C_{16}H_{18}N_3SCl$). It dissolves in water to form an intensely blue solution, thus serving as its own indicator. It is readily reduced by titanous chloride to methylene white in accordance with the equation:

$$C_{16}H_{18}N_3SCl + 2H = C_{16}H_{20}N_3SCl$$

A solution is made containing about 4 grams of the pure dyestuff per liter. This is standardized against titanous chloride solution by direct titration in an atmosphere of carbon dioxide. The complete decolorization of the dyestuff indicates the end point. The titration must be carried out above 35°C or a drop of 10% sodium salicylate added to insure a sharp end point.

Standard Potassium Dichromate Solution

A decinormal solution of this salt may be prepared by weighing out 4.903 grams of the pure salt, dissolving it, and diluting the solution to one liter. The salt must be dried at 400°C in a platinum crucible to get rid of the last traces of moisture. After cooling, the fused mass is crushed in an agate mortar, transferred to a glass stoppered bottle, and weighed by difference.

The value of this solution is checked using pure iron wire. The sample of iron is dissolved, converted to the sulphate, oxidized with

permanganate, reduced by zinc, and titrated with the dichromate solution using potassium ferricyanide as outside indicator.

Standard Copper Sulphate Solution

About 67 grams of hydrated copper sulphate is dissolved in water and made up to a liter. This is standardized by measuring 10cc samples into 100cc beakers, adding 1cc of concentrated sulphuric acid and 1cc of 6N-nitric acid, diluting to 60cc, and plating out the copper on a weighed platinum electrode.

Standard Molybdate Solution

A solution of phosphate is standardized by precipitating with ammonium molybdate reagent, dissolving the precipitate of phosphomolybdate, reprecipitating the phosphoric acid with magnesia mixture, igniting the precipitate, and weighing as the magnesium pyrophosphate.

By the use of standard phosphate solution, molybdenum is precipitated in known quantities as ammonium phosphomolybdate, dissolved, and diluted in a graduated flask. The size of the molybdenum sample is determined by the portion of this solution taken.

Determination of Molybdenum

The molybdenum is reduced to the trivalent state with zinc and hydrochloric acid according to the procedure given by Thornton & Elderdice (25). The reduced solution is titrated directly with methylene blue solution in an atmosphere of carbon dioxide. The end point is indicated by the blue green of the $MoCl_5$ and the first excess of methylene blue. The valence change of the molybdenum is from three to five.

Standardization of the Titanous Chloride Solution with Standard Permanganate Solution

A measured volume of the standard permanganate solution is added to an excess of ferrous ammonium sulphate in dilute sulphuric acid. A quantity of ferrous iron equivalent to the permanganate added is oxidized to the ferric state. An excess of ammonium thiocyanate is added as indicator. The iron is reduced with titanous chloride in an atmosphere of carbon dioxide. The titanous chloride used is equivalent to the permanganate. It is necessary to run a blank on the ferrous ammonium sulphate.

Standardization of the Titanous Chloride Solution with Standard Dichromate Solution

A measured volume of the standard dichromate solution is added to an excess of ferrous ammonium sulphate in dilute sulphuric acid solution. Ammonium thiocyanate is added (10cc of 10%). The ferric iron formed is reduced in an atmosphere of carbon dioxide with titanous chloride. The end point, disappearance of the red of the ferric thiocyanate, is not obscured by the light green of the chromic sulphate.

Standardization of Titanous Chloride Solution with Standard Copper Sulphate Solution

To a measured volume of the standard copper sulphate solution is added a small measured volume of standard ferric alum solution. A considerable excess of hydrochloric or sulphuric acid is added with a large excess of thiocyanate indicator. Water is added until a volume of about 150cc is obtained. Titrate cold with titanous chloride in an atmosphere

of carbon dioxide. The copper is precipitated in the form of the white cuprous salt. The end point is the disappearance of the red color and corresponds to the reduction of the cupric to the cuprous salt and the reduction of the ferric to the ferrous ion.

RESULTS OF EXPERIMENTS

The following table indicates the stability of titanous chloride solution when prepared and stored in accordance with the method given.

TABLE I

Expt. No.	Date	Ferric Alum taken c. c.	$TiCl_3$ required c. c.
1.	Jan. 5, 1933	25.01	32.64
2.	Jan. 15, 1933	25.01	32.66
3.	Feb. 16, 1933	25.01	32.61
4.	March 25, 1933	25.01	32.63
5.	May 13, 1933	25.01	32.61
6.	May 17, 1933	25.01	32.62

Excellent agreement was shown in the values obtained by various methods for standardizing the titanous solution.

TABLE II

Standard	Standardized by:	Normal value of $TiCl_3$
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	———	0.06219
Std. $KMnO_4$ Soln.	Sodium Oxalate	0.06223
Std. $K_2Cr_2O_7$ Soln.	iron wire	0.06218
Std. $CuSO_4$ Soln.	electrolytically	0.06221

No crystalline copper sulphate could be found which gave consistently precise values for the normality of the titanous chloride. Even the special grades of copper sulphate were found by electrolytic determinations as low as 98.8% $CuSO_4 \cdot 5H_2O$. No definite purity factor was found for any brand used; the copper content of the salt varied appreciably from bottle to bottle. Electrolytic determinations of copper agreed

with those using titanous chloride when the copper salt was dissolved and the samples taken from the same solution.

Small quantities of molybdenum may be precisely determined by the use of standard methylene blue solution.

T A B L E III

Molybdenum taken grams	Molybdenum found grams	error parts /1000
.01242	0.01238	-3.2
.01366	0.01360	-4.6
.01490	0.01491	+0.7
.01615	0.01601	-9.
.01739	0.01716	-25.
.01863	end point obscured	

DISCUSSION AND CONCLUSIONS

The stability of the titanous solution when kept under hydrogen has been demonstrated by all workers who have used the reducing agent. The apparatus is simple, rugged, and requires little care.

No special reagents are required for satisfactory standardization. Since all the iron must be converted to ferric, the oxidation of a small amount of the ferrous iron in the ferrous ammonium sulphate prior to weighing does not decrease the precision of standardization to an extent which should bar its use. Standard permanganate solution or dichromate solution is often at hand. The oxidation of the ferrous salt with the oxidizing agent and subsequent reduction of the ferric iron is the simplest conceivable method. Direct titration of the permanganate with titanous chloride was not found to be satisfactory even in the presence of a large quantity of manganous sulphate. Knecht and Hibbert (26) suggest the addition of an excess of the reducing solution to the chromic acid and back titrating the excess using standard iron alum solution. Ammonium thiocyanate is oxidized by chromic acid as well as by permanganate; thus its use in their presence is prohibited.

Any objections raised concerning the use of copper sulphate as a standard must be directed against the salt and not against the reaction between the cupric ion and the titanous ion. If care is taken to secure a definite quantity of cupric salt and the reduction is carried out in dilute acid solution, the end point corresponds to the stoichiometrical equation. Even freshly crystallized cupric sulphate could not be prepared in which the copper content corresponded with the formula. Copper sulphate solution had been standardized either iodiometrically or electro-

lytically proved to be a good standard for the titanous chloride solution.

Knecht and Hibbert (27) show data for the determination of samples of molybdenum from 0.03 to 0.05 gram. Thornton and Elderdice (28) indicate that the green of the molybdenum pentachloride obscures the end point when samples of this size are used. Around .015 gr of molybdenum is the largest sample with which the latter experimenters were able to work and secure a definite end point. The results of this work upheld their observations. Except in cases when it is definitely known that the amount of phosphorus to be determined is small, the standard gravimetric procedure is to be recommended.

The determination of glucose, hydrogen peroxide, chlorate, persulphate, picric acid, and indigo has been carried out according to the directions given by Knecht and Hibbert (29). In no case has much difficulty been found in duplicating the procedures.

Experimental work upon the many classes of compounds which may be estimated makes it evident that titanous chloride is the most important of all the reducing agents at our disposal for volumetric analysis. The permanence of the solution when it is properly stored cannot be doubted. The standardization of the solution requires no rare or expensive chemicals. With a tank of liquid carbonic acid gas at one's disposal the titrations are slightly more difficult to carry out than those in an open container. The end points are usually sharp; only occasionally are they fugitive. Since the titrations themselves require little time, several students might use the same set up during a laboratory period. Thus one or two stock bottles of the solution might be used by an entire

class within the space of a few weeks. Titanous chloride solution might well be used as a standard reagent by elementary and intermediate classes in volumetric analysis.

S U M M A R Y

1. This work shows that titanous chloride solution may be profitably introduced as a standard reducing agent for use in classes in elementary quantitative analysis.

2. Copper sulphate cannot be assumed to contain its formula weight of copper. The titanous chloride solution used to reduce cupric salts corresponds to that required by the stoichiometrical equation.

3. The indirect estimation of phosphorus by precipitating it as ammonium phosphomolybdate, dissolving the yellow precipitate, reducing the molybdic acid with zinc and hydrochloric acid, and titrating the molybdenum trichloride formed with standard methylene blue solution is satisfactory only when small quantities of that element (phosphorus) are involved.

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B I O G R A P H Y

The author was born in Washington, D. C., July, 1911. All school work prior to his senior year of high school was done at Asherton, Texas. He was graduated from Sperryville High School, Sperryville, Virginia, in June, 1928. He received the degree of Bachelor of Science from the College of William and Mary in September, 1932. He returned to William and Mary for the 1932-33 session as an assistant in the Chemistry laboratory; and, during the session of 1933-34, he was an instructor in chemistry at the same school.